DECAY AND RELAXATION OF CORE HOLE STATES IN MOLECULES

by

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Institute of Physics
Uppsala 1979

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ABSTRACT

Instrumentation work for obtaining highly resolved soft X-ray emission spectra of free atoms and molecules is described. Two instruments have been built which use concave reflexion gratings, 3 m and 10 m respectively, mounted at grazing incidence. The X-ray emission is induced from flowing gas samples by an electron beam and spectra are recorded by means of photographic and photoelectric detection. The spectra are calibrated with optical XUV transitions from highly ionized atoms.

Soft X-ray emission spectra of molecules containing atoms from the second and third periods are recorded and analyzed in terms of molecular orbital theory. The spectra yield information on symmetry and localization properties of valence orbitals and of binding energies and chemical shifts of the initial core hole states. Vibrational fine structure has been discerned in several spectra, and from the analyses of these vibrational bands information on the core hole state potential energy surface is derived. Soft X-ray satellite spectra are investigated, which give information on energies, populations and lifetimes of multiply ionized inner hole states.

Computational investigations utilizing ab initio methods are performed for various phenomena associated with the formation of a deep core hole. These can be summarized as: Correlation and relaxation effects in ESCA, Auger and shake-up spectra of H_2O: Role of relaxation,exchange interaction and localization in formation of core ESCA and X-ray band profiles of diatomic molecules; Calculation of core hole potential energy surfaces and vibrational excitations in ESCA and X-ray spectra of small polyatomic molecules; X-ray transition moments, d-orbital participation and validity of one-center intensity model for SF_6.

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INTRODUCTION

Much of the early progress in our understanding of the atom was derived from the use of X-ray spectroscopic methods. A variety of techniques utilizing X-ray emission or absorption have been developed through the years, and they have found a multitude of applications in various fields of scientific endeavour. For the most part, X-ray emission spectroscopy has been used for the study of the electronic structure of matter in the solid phase. Gas phase studies, on the other hand, were not initiated until some ten years ago. The early gas phase experiments made it evident that one needed higher resolution in order to secure information about core and valence electronic structure of the molecules. This thesis presents experimental work for obtaining highly resolved soft X-ray emission spectra of free atoms and molecules. The spectra obtained provide a wealth of experimental data which have not been revealed in previous X-ray emission spectra. The thesis contains theoretical analyses of the experimental results and also presents computational studies of other processes that are related to inner shell ionization. These studies concern the role of relaxation and correlation in Auger, ESCA and vibrational shake-up spectra.

The thesis is based on the following papers of which a summary will be given below:

1. An instrument for high resolution studies of molecular soft X-ray emission spectra: J. Nordgren, H. Ågren, C. Nordling and K. Siegbahn, Ann. Acad. Reg. Sci. Uppsaliensis, No 21 (1978).

2. A new 10 m grazing incidence instrument for molecular X-ray emission studies: J. Nordgren, H. Ågren, L. Pettersson, L. Selander, S. Griep, C. Nordling and K. Siegbahn, UUIP-1002, April 1979.

3. X-ray emission spectra of small molecules: L.O. Werme, J. Nordgren, H. Ågren, C. Nordling and K. Siegbahn, Z. Physik, 272, 131 (1975).

4. High-resolution X-ray emission spectrum of gaseous oxygen: J. Nordgren, H. Ågren, C. Nordling and K. Siegbahn, J. Phys. B, 10, L511 (1977).

5. X-ray spectra and core hole energy curves of some diatomic molecules: H. Ågren, L. Selander, J. Nordgren, C. Nordling, K. Siegbahn and J. Müller, Chem. Phys. 37, 161 (1979).

6. X-ray emission spectra of NH_3 and N_2O: J. Nordgren, H. Ågren, L.O. Werme, C. Nordling and K. Siegbahn, J. Phys. B, 9, 295 (1976).

7. Vibrational excitations in soft X-ray emission and core ESCA spectra of NH_3: H. Ågren, J. Müller and J. Nordgren, UUIP-990, Nov. 1978.

8. The X-ray emission spectrum of water: J. Nordgren, L.O. Werme, H. Ågren, C. Nordling and K. Siegbahn, J. Phys. B, 8, L18 (1975).

9. A basis set investigation for the oxygen 1s ionization potential in H_2O: H. Ågren, S. Svensson and U.I. Wahlgren, Int. J. Quant. Chem. 11, 317 (1977).

10. SCF and limited CI calculations on the 1s shake-up spectrum of H_2O: S. Svensson, H. Ågren and U.I. Wahlgren, Chem. Phys. Letters, 38, 1 (1976).

11. SCF and limited CI calculations for assignment of the Auger spectrum and of the satellites in the soft X-ray spectrum of H_2O: H. Ågren, S. Svensson and U.I. Wahlgren, Chem. Phys. Letters, 35, 336 (1975).

12. Semiinternal correlation in the Auger electron spectrum of H_2O: H. Ågren and H. Siegbahn, UUIP-1003, March 1979.

1 Ab initio investigations of vibrational excitations in the photoelectron spectra of H_2O. Comparison of different methods: H. Ågren and J. Müller, UUIP-996, Jan. 1979.

14. Role of localization in the prediction of core ESCA line shapes of N_2, O_2 and NO: H. Ågren, J. Müller and O. Goscinski, Chem. Phys. 38, 000 (1979).

15. Calculation of vibrational structure in core and valence ESCA spectra of CO and N_2: J. Müller and H. Ågren, UUIP-997, March 1979.

16. Valence electron structure of the SF_6 and CS_2 molecules, studied in high resolution X-ray emission: H. Ågren, J. Nordgren, L. Selander, C. Nordling and K. Siegbahn, Physica Scripta 18, 499 (1978).

17. Multiplet structure in the high-resolution X-ray emission spectrum of neon: H. Ågren, J. Nordgren, L. Selander, C. Nordling and K. Siegbahn, J. Electron Spectrosc. 14, 27 (1978).

18. Lifetimes of inner shell multiple vacancy states in argon: J. Nordgren, H. Ågren, L. Selander, C. Nordling and K. Siegbahn, Physica Scripta, 16, 70 (1977).

19. An X-ray emission study of inner levels in multiply excited argon: J. Nordgren, H. Ågren, C. Nordling and K. Siegbahn, Physica Scripta 19, 5 (1979).

20. Electron spectroscopy and ultra-soft X-ray emission of free molecules: J. Nordgren, H. Ågren, L. Selander, C. Nordling and K. Siegbahn, Physica Scripta 16, 280 (1977).

I. The instruments

For detailed studies of valence electron structure of free molecules in X-ray emission, it is necessary to avoid the involvement of initial states of too large a width. Therefore, it is preferable to study X-ray transitions connecting valence states with the outermost core states. This radiation, i.e. K radiation for the second period elements, L radiation for the third period elements etc. has wavelengths of 1-20 nm, i.e. it falls in the soft or ultrasoft X-ray region.

The two experimental approaches that have been used for investigation of soft X-ray emission from molecules are based on wavelength dispersion either by means of crystals or by means of gratings. Artificial soap film crystals, in which the quasi-atomic plane distances are sufficiently large to permit Bragg reflection, have been widely employed,[1,2,3] however, manufacturing difficulties limit the number of diffracting atomic planes to about 60. As a consequence, the resolution attained in these studies has been too low to allow finer details of the spectra to be discerned.

The approach described in this work employs precision ruled or holographic reflexion gratings in a Rowland mounting. In order to attain sufficient diffraction efficiency the angle of incidence must exceed the cut-off angle for the actual wavelength, which means in this case that the angle of incidence must be greater than 85°. This approach is referred to as the "grazing incidence technique". The main advantage with this technique as compared to the soap film crystal technique is its much higher resolution capability. With a grazing incidence analyzer it is possible not only to separate the valence electron levels in a molecular X-ray spectrum but also to resolve vibrational fine structure within the X-ray bands. The reali-

zation of a grazing incidence molecular X-ray spectrometer which incorporates the features to be described below has been documented in paper 1 of this thesis.

The considerable improvement in resolution (up to two orders of magnitude) attained with the grazing incidence technique is counterbalanced by a sacrifice of intensity, and introduces tedious adjustment procedures. The latter problem can be alleviated with a set of auxiliary mechanical and optical devices for adjustment of the analyzer, without resorting to tedious exposures in situ. The X-ray source of the instrument must be of considerable intensity in order to compensate the low transmission of the grazing incidence analyzer. The low transmission is a combination of low grating reflectivity at these wavelengths and low acceptance angle. Therefore direct electron impact has been used for excitation of spectra. This is accomplished by means of three stage differential pumping which allows the use of a sample pressure in the collision chamber of about 0.2 kPa while simultaneously maintaining high vacuum (0.1 mPa) at the filament of the electron gun. In order to attain sufficient X-ray intensity the required current density in the collision chamber is of the order of 1 A/cm^2. Three focusing magnetic lenses direct the 100 mA, 10 kV electron beam through the orifices which separate the differential pumping compartments and through the collision chamber. The sample gas flows through the collision chamber at a high rate to reduce the contributions from molecular fragments of dissociated molecules to the X-ray spectrum.

Apart from a rather detailed description of the molecular X-ray instrument, which incorporates a 3 m grazing incidence analyzer, paper 1 also presents an adjustment procedure in which the mutual dependence of the various steps of adjustment is minimized. A brief recapitulation of concave grating theory is given and the practical applications of the theory on the design of the dispersive system are pointed out. The influence on resolution and intensity of

various instrumental settings in terms of slit width, type of grating and grating coating material, groove height, groove separation and angle of incidence are discussed and the conclusions reached are substantiated by numerical calculations and experimental results.

The detection of X-rays has mostly been carried out by means of photographic plates with high-sensitive emulsions. Photographic detection has some important advantages not the least of which is the fact that it covers a large wavelength region. We have exploited this feature for calibration purposes by superimposing on the same plate optical XUV spectra or X-ray spectra in different orders from different molecules. Photographic detection is preferable when the ultimate resolution of the spectrometer is to be exploited. The main disadvantage of photographic detection is the non-linear intensity response of the emulsions which introduces errors, especially when recording lines of either very high or very low intensity. A one-channel photoelectric detection system has therefore been incorporated with the instrument. In order to account for instabilities in source intensity the step increments of the detector along the Rowland-circle is controlled by another detector placed at the focus of the zeroth order reflected radiation.

A sliding spark device was built for generation of optical XUV transitions in highly ionized atoms to be used for calibrating the soft X-ray spectra. The energies of these XUV transitions are known with high accuracy, having been ultimately calibrated to well established reference lines. Since the energies of the final valence hole states of the soft X-ray transitions are often accurately known from optical or UV ESCA spectroscopy this calibration procedure provides a means for very precise determinations of inner electron binding energies and chemical shifts.

Some time ago the construction of a new molecular X-ray spectrometer was initiated. The new instrument was intended to follow the same principles as the first instrument but incorporating several important improvements as regards X-ray source intensity, instrument transmission, resolution of the analyzer and convenience of instrument operation. The new X-ray source consists of a four-stage differentially pumped X-ray tube with gas cell target. The non-rotationally symmetric electron beam is focused and aligned through the slits of the tube by means of micro-processor controlled magnetic quadrupole magnets. Adjustment of the grazing incidence analyzer is reduced to a single adjustment of the radius of curvature of the grating by means of elastic deformation. The resolving capability of the new instrument has been substantially increased by the large radius of curvature of the grating (10 m) and by the increased intensity of the X-ray source which allows recordings of spectra in higher orders. Paper 2 gives a first report on the progress of the work with this instrument. The paper briefly describes the instrument and presents recordings of a soft X-ray emission spectrum of argon as well as a recording of a spark discharge induced XUV spectrum from the calibration light source. These spectra were recorded with an instrument resolution of about 8 mÅ which corresponds to an energy resolution of 33 meV in the argon spectrum.

II. High resolution soft X-ray emission studies of free molecules

X-ray deexcitation connects a localized core vacancy state with a valence vacancy state via electromagnetic dipole interaction. This imposes simple selection rules for the allowed symmetries of the states involved. In many compounds different core hole states on the same or different atomic centers can be formed. These core states are in general well separated in energy and since they often de-

fine different symmetries, different constraints are placed on the allowed dipole transitions from the common set of valence orbitals. Hence symmetry assignments and ordering of these valence orbitals can often readily by deduced by analysis of the soft X-ray spectra. Furthermore, for the large body of free molecules formed by atoms in the second period the soft X-ray transitions are to a large extent confined to the atom in which the core hole is localized. Through the application of the MO-LCAO scheme (Molecular Orbitals as Linear Combinations of Atomic Orbitals) this one-center property also introduces atomic selection rules into the analysis of the soft X-ray emission spectrum. The soft X-ray band intensities "map" the local properties of the wave function, for example in K-emission spectra the intensities are determined by the local p-character of the valence orbitals.[4] Investigations utilizing wave functions computed with semiempirical methods have been shown to be successful for a qualitative description of the elements. For these low Z elements valence X-ray photoelectron spectra provide complementary information, since the cross section for ionization of 2s electrons is much larger than for 2p electrons.

In paper 3 various analytical aspects of molecular soft X-ray emission spectra are briefly outlined and exemplified by the K-emission spectra of CO, N_2, NO and CO_2. The connection between molecular localization properties and soft X-ray emission intensities are illustrated by the carbon K and oxygen K spectra of CO. The relative intensities of the bands are quite different in the two spectra. The outermost 5σ orbital has a much larger carbon 2p than oxygen 2p character and appears therefore much stronger in the carbon spectrum. The opposite applies for the 4σ orbital, whereas the 1π orbital is sufficiently delocalized over the two atomic sites to be represented with considerable intensity in both spectra. The influence of X-ray symmetry selection rules is exemplified by the CK and OK

spectra of CO_2. Vibrational fine structure is resolved in several of the recorded bands of N_2, CO and NO. Electron versus photon impact is discussed in terms of excitation efficiency and technical performance.

Paper 4 reports the K X-ray emission spectrum of the open-shell molecule O_2, which presents an additional feature of multiplet splitting. The interpretation of this spectrum has been facilitated by the use of electron spectroscopic data for the initial and final states of the X-ray transitions. The spectrum exhibits a rather prominent satellite structure.

X-ray emission spectroscopy is also useful for studying potential energy surfaces (equilibrium geometries and force constants) of core ionized states. Core electrons have generally been regarded as non-participating in the formation of chemical bonds due to their negligible overlap with orbitals from neighbouring atoms. Recent theoretical investigations[5] have, however, proposed substantial differences in molecular equilibrium geometries between the neutral ground state and the core hole state species. A correct treatment of relaxation has turned out to be decisive not only for the magnitude but also for the direction of these differences. High resolution ESCA investigations utilizing X-ray monochromatization have revealed asymmetric band features in the core spectra.[6,7] These features have been attributed to vibrational excitations, which is in accordance with the theoretical findings. In X-ray emission, the band profiles will depend on the shapes and relative positions of the ground, core hole and valence hole state energy surfaces. The high resolution has in several cases allowed the separation of closely lying vibrational structures in the X-ray bands. The vibrational fine structures revealed in the X-ray spectra of the diatomic molecules presented in paper 3 and 4 are analyzed in paper 5. It is demonstrated that the position and form of the intermediate core hole

state energy surface has a profound influence on the final X-ray band envelope. From the measured spectra of the CO and N_2 molecules and from Franck-Condon (FC) analysis, where experimental data are used for the ground and valence hole states, it was possible to deduce accurate values for equilibrium geometries and harmonic force constants for the Cls and Nls core hole states respectively. The inclusion of anharmonicity in the analysis gives a small change (approximately 1 pm) to the best fitted value for the core hole state equilibrium geometry. These results are compared with data obtained from the frozen orbital approximation, the equivalent core approximation and from self-consistent field calculations. The latter are shown to reproduce the measured X-ray vibrational profile quite well. A qualitative investigation is performed for the X-ray spectra of the $\overset{*}{CO}$, $\overset{*}{NO}$ and $\overset{*}{O}_2$ species. The analysis of the open-shell NO and O_2 molecules is slightly more complicated due to the presence of numerous satellites among the main lines and, from a computational point of view, the need to introduce many-determinant wave functions.

Paper 6 presents the K X-ray emission spectra of the small polyatomic molecules N_2O and NH_3. In accordance with its delocalized 2p-character the 1π orbital in N_2O is observed in the spectra pertaining to all the three different core hole states. In the NH_3 spectrum two main bands and a number of satellites are observed. The le band shows an unusual broad feature, which is associated with the bonding character of this orbital and with Jahn-Teller instability. The $3a_1$ band shows some intrinsic structure which in comparison with the corresponding UV ESCA spectrum suggests excitation of stretching vibrations. The vibrational structure in this X-ray band is further investigated in paper 7 together with a similar analysis for the Nls core ESCA band. The results of the performed ab initio investigations show that the Nls and $3a_1$ hole states both are planar and that the N-H bond distance of the former

state is considerably shorter than that of the ground state. Various kinds of Franck-Condon calculations are performed for the N1s ESCA band, which are all consistent in that they describe this band as dominated by a progression of closely spaced vibrational peaks of the pure bending mode. The computed $3a_1$ X-ray bond profile shows a more complex feature, in which many stretch-bend combination levels are excited. A comparison between the computed and the experimental band profiles gives support to the validity of the calculated energy surface of core hole state.

III. Computational studies on the formation and decay of molecular core hole states

The H_2O molecule has in this thesis been chosen as the object for investigations of various phenomena associated with the formation and decay of a deep core hole. This molecule constitutes a simple polyatomic system, small enough to be suitable for extensive computational studies utilizing non-empirical methods. The K X-ray emission spectrum of H_2O is reported in paper 8. The three main lines are straightforwardly assigned to their respective molecular valence orbitals. In addition, this spectrum shows a rich satellite structure. On the basis of calculations described in papers 10 and 11 one can assign these satellites to three different types of processes:

(i) $3a_1^{-1}a_1$ and $1b_1^{-1}a_1$ transitions in the doubly ionized molecule,

(ii) resonance transitions in the neutral molecule, and for the most energetic satellite;

(iii) transitions connecting a shake-up state with a valence hole state.

Much of the recent progress in the field of molecular ab initio calculations can be associated with the use of finite basis sets of atomic optimized contracted Gaussian

type orbitals. The contractions are carried out with the purpose of maintaining maximum flexibility for the more diffuse orbitals describing the valence shells, whereas the core orbitals, which presumably do not respond to the molecular formation to the same extent, are rather heavily contracted. In ΔE_{SCF} calculations of core ionization potentials and Auger and X-ray transition energies an additional amount of flexibility is required for the outer orbitals in order to account for the relaxation following the core hole formation. As a prerequisite for the calculations described in papers 10-13, a basis set investigation for the core 1s ionization potential in H_2O was undertaken in paper 9. The question of whether it is advantageous to employ basis functions optimized for the Z+1 atom was also investigated.

The development in ESCA instrumentation, incorporating high power excitation, X-ray monochromatization, and multichannel detection, has greatly facilitated studies of electronic reorganization following core ionization. With higher resolution and improved signal-to-background ratio it has been possible to determine accurate energies and intensities for satellites in a number of core electron spectra, which in turn has generated interest for theoretical investigations of these structures. Paper 10 reports self-consistent field (SCF) and limited configuration interaction (CI) calculations on the 1s shake-up spectrum of H_2O. A computationally convenient way to proceed for calculating shake-up energies is to perform an SCF calculation on the core hole state followed by a CI comprising all single excitations from the valence shells. This approach gave, however, energies in agreement with the spectrum only for the shake-up peaks of lowest energy and the wave functions obtained were difficult to interpret in terms of orbital excitations. This may be explained from the neglect of response of the orbitals to the valence hole (relaxation). Energies and intensities, the latter obtained by adopting the sudden approximation, were therefore also determined by SCF calculations on one

or both doublet states of the different shake-up configurations. These SCF calculations were followed by two types of limited CI calculations; the first consisted of a 2 x 2 CI between the two doublets and for the second approach an internal valence CI was carried out. Both methods gave energies in good agreement with experiment. Intensities, however, were found to be reasonable and relatively independent of the choice of molecular orbital basis only for the internal valence CI.

The overwhelming majority of transitions in inner-shell ionized low-Z species are radiationless, because the X-ray deexcitation process has a comparatively low probability. The radiationless transitions (i.e. Auger transitions) connect the discrete ion inner hole state to a state with two vacancies in outer shells and one electron in the continuum. Molecular Auger electron spectra are rather complicated to interpret for the light elements belonging to the second period of the periodic table because the valence orbitals are involved in the transitions. Of the Auger spectra[8] pertaining to the second period hydrides, the spectrum of the water molecule shows the most detailed structures and was therefore chosen as the object for the investigation undertaken in paper II. As shown in the paper, orthogonality constrained SCF calculations employing Roothaan's many-operator open shell formalism[9] yield poorly converged energies for singlet states with two open shells of the same symmetry. This is corrected by means of internal CI calculations involving the interacting states. The SCF results for other than the $^1A_1$ states were unaffected by inclusion of this type of CI. The final results for the Auger transition energies together with a quasiatomic intensity model[8] provide a straightforward assignment of the observed structures, however, the assignments of the two low kinetic energy bands are somewhat ambiguous. The calculation attributes a very weak band to the $2a_1^{-2}$ transition, which according to the intensity model should be rather

strong, whereas a stronger band 6 eV higher in kinetic energy is unaccounted for. In paper 12 an attempt is made to solve this ambiguity by enlarging the previous calculation with a semiinternal CI for the $2a_1^{-2}$ transition. This investigation was motivated by previous studies of inner valence ESCA spectra where these types of CI resonances have been found to provide an explanation for some unusual broad features of the peaks.[10] The semiinternal configurations are constructed by a one-electron redistribution from the outer to the inner valence shells coupled with a promotion of one electron to the unoccupied space. Indeed it was found that these resonances were very strong for the $2a_1^{-2}$ state and one eigenvalue of the CI calculation was found at the position of the previously unassigned band at 456 eV. Energies for initial and final state shake-off satellites were also calculated. It was found that the position of the shake-off edges pertaining to the strong $1b_1^{-2}$ and $3a_1^{-1}$ $1b_1^{-1}$ transitions also were located at 456 eV and must therefore also be considered in the assignment of the band.

The series of investigations of the water molecule undertaken in this thesis is completed with paper 13 in which results from computational studies of the vibrational structure in the O1s and $1b_1$ ESCA bands are presented. Two different schemes for calculating vibrational intensities are considered. The relationship between these schemes and the demands for precision in the calculation of energy gradients and force fields are investigated. Force fields and equilibrium geometries of the ionized and neutral states obtained from Hartree-Fock calculations provide sufficient ingredients for a successful reproduction of both the O1s and the $1b_1$ vibrational profiles. Inclusion of relaxation is important when computing core state vibrational excitations from the energy gradients. The influence of relaxation on core ESCA line shapes is further elucidated in paper 14, which reports vibrational excitations and energy surfaces for the core ionized species of NO, O_2 and N_2.

It is shown that the changes in equilibrium bond lengths following core ionization follow the expected pattern; namely a shortening for the N1s ionized species and a significant lengthening for the O1s ionized species, the lengthening being associated with a corresponding decrease in force constants. However, energy gradients and equilibrium geometries differ substantially for the different multiplet components of the core ionized paramagnetic O_2 and NO molecules, with a longer bondlength for the lower multiplet, and this is reflected in the theoretically constructed band profiles. For the homonuclear O_2 and N_2 molecules there are two equivalent atomic sites over which the core hole may be delocalized. The Hartree-Fock calculations performed on the delocalized ion yield a bond length which is too short, leading to vibrational excitations for the core state at variance with observations in ESCA and X-ray spectra.

Paper 15 presents a computational investigation of the vibrational excitations in the core and valence ESCA bands of CO and N_2. Franck-Condon factors obtained from optimized geometries and force constants of the neutral ground and ionized states are compared with those obtained directly from calculated ionized state energy gradients. Geometries, force constants and energy gradients are calculated both from frozen orbital energies and open-shell restricted Hartree-Fock (OS RHF) wave functions. The results of the different methods employed are discussed in relation to the experimental data.

The X-ray investigations discussed so far have been confined to studies of K-emission from the second period of the periodic table. The sulphur L-emission spectra of SF_6 and CS_2 reported in paper 16 present the first high-resolution studies of molecular soft X-ray emission from elements in the third period. The SF_6 spectrum is recorded with a high-dispersive holographic grating yielding a reso-

lution of approximately 5000 for the first order sulphur emission. A comparison of the sulphur L spectra with the fluorine K and carbon K spectra from the SF_6 and CS_2 molecules respectively, clearly demonstrates the symmetry selection imposed by the dipole character of the soft X-ray emission. Ab initio calculations of the transition moments are performed for the sulphur L spectrum of SF_6 from which two conclusions are drawn. Firstly, inclusion of d-orbital participation in the chemical bonding influences the transition moments very sensitively and agreement with experimental intensities is obtained only when this inclusion is properly considered. Secondly, the one-center intensity model, successfully employed in the study of molecules formed by second period elements, does not hold for L-emission in SF_6, and a full molecular orbital treatment of the intensities is required in this case. A group of very narrow satellite lines are suggested to correspond to transitions in multiply ionized sulphur. Possible mechanisms for creation of the initial states of these transitions are discussed.

IV. X-ray emission satellite studies

The earliest X-ray spectroscopic investigations gave evidence of weak "satellite" lines in the neighbourhood of the main lines.[11] These satellite lines were also called "non-diagram" lines, since their energies could not be expressed as term differences of the one-vacancy energy level diagram of the emitting atom. The X-ray satellites can be put into different categories according to the origin. The most commonly occurring type of satellite line corresponds to one-electron transitions within the doubly (multiply) ionized atom or molecule (so-called Wentzel-Druyvesteyn satellites). These satellites provide information on energies, populations and lifetimes of multiply excited inner hole states. The satellite energies relative to the main transitions will depend on which shell the "spectator" hole is localized. Most of these satellites are found in the high energy part

of the X-ray spectrum. For either electron or photon excited K-emission spectra, the initial state of the satellite transition is formed by shake-off or shake-up processes accompanying the core ionization. For high energy excitations, the integrated satellite intensities will to a large extent be independent of the excitation agent. For strongly correlated systems, however, this does not seem to hold,[12,13] e.g. hypersatellites corresponding to ionization and shake-off in the same shell will have different intensities in photon and electron excited spectra.

In soft X-ray emission from higher Z elements the initial doubly or multiply ionized states can also originate from Auger and Coster-Kronig cascades from higher lying states created in the primary ionization. The onset of energetically possible Coster-Kronig transitions is always accompanied by strong satellite intensities. Other types of high-energy satellites, which are especially strong in electron excited soft X-ray emission spectra, are due to transitions in the neutral molecule. These transitions connect the ground state with a configuration where a core hole electron is excited to an unoccupied orbital. This type of transitions will have direct analogues in X-ray absorption or electron energy loss spectra.

The low energy part of the soft X-ray spectrum generally exhibits a rich satellite structure, although not as intense as the initial state shake-off satellites appearing in the high energy part. The structure contains both discrete lines and continuous intensity distributions. The discrete lines give evidence of so-called "radiative electron rearrangements" (RER), referring to the simultaneous process of X-ray emission and electron redistribution in the valence shells, whereas the continuous intensity distributions represents "radiative Auger" transitions analogous to the Auger process. The possibility of accounting for these satellites in the independent particle model by means of

monopole shake-up or shake-off calculations is rather limited. In fact, inclusion of correlation in the initial as well as in the final state is found to be crucial for an adequate description of this satellite structure.[14] This is in analogy with observations for valence photoelectron satellite spectra.[15] The high resolution attained in soft X-ray spectra allows a direct comparison with UV ESCA spectra with respect to these correlation satellite structures. These two types of spectra are analogous to some extent (see Ar, Ne and N_2 spectra) but differ with regard to relative intensities and to the appearance of certain peaks, which can be attributed to the fact that the initial states of the two processes are different.

Paper 17 presents the high resolution K-emission spectrum of neon recorded in the first to the fifth orders. Disregarding the final state correlation satellites on the low energy side and a hyper-satellite on the far high energy side, the spectrum can be subdivided into five regions, each region corresponding to a particular charge state of the neon ion which was initially created by multiple shake-off processes. The multiplet structure for the transitions pertaining to the doubly charged shake-off states has been resolved. From the measured intensities of the multiplets and from calculated term fluorescence yields it has been possible to derive values for the 2s/2p shake-off ratio and for the relative populations of the different initial terms. It is found that for the $1s^{-1}2p^{-1}$ configuration the $^3P/^1P$ population ratio is non-statistical which is in accordance with observations in Auger spectra[16] and with recent shake-off calculations including continuum interchannel coupling.[17] Using calculated fluorescence yields and statistical arguments for multiple shake-off probabilities it has been possible to construct a theoretical spectrum for the X-ray transitions pertaining to the triply ionized atom which is found to reproduce the main features of the experimental spectrum. Using optical data for the final levels of the composed

$K\alpha_{1,2}$ peak the neon 1s binding energy is determined with an accuracy of ±0.05 eV.

X-ray emission studies yield information on lifetimes of inner shell single or multiple vacancy states, provided the attained resolution is sufficiently high. According to the theory of Wigner and Weisskopf[18] the lifetime widths of the individual hole states should contribute additively to the width of the emitted X-ray. Since the final states of soft X-ray transitions involve vacancies in the valence shell the emission linewidth is almost exclusively determined by the lifetime of the initial state. This in turn is determined by the Auger rate (or Coster-Kronig rate when these transitions are energetically allowed) due to the very low (soft X-ray) fluorescence yield. When determining the linewidths, the spectrometer broadening can be directly accounted for by recording spark induced optical XUV lines which are extremely sharp in comparison with the X-ray lines. From the measured 5th order neon $K\alpha_{1,2}$ line, a value for the lifetime of the 1s hole state is derived, which is found to agree with core ESCA measurements.[19] The initial state width does not seem to vary much going from singly to multiply ionized states, in contrast to the observed result for L-emission in argon. Paper 18 shows that linewidths for transitions arising from the $2p^{-1}3p^{-1}$ initial hole states in argon are considerably smaller than for those from the $2p^{-1}$ or $2s^{-1}$ hole states (the latter showing an additional Coster-Kronig broadening). Moreover, the linewidths show significant variations among the various terms. These intraconfigurational linewidth variations, which refer to a corresponding change in Auger rate for the initial states, are not well reproduced in current computational investigations. In the case of molecules the vibrational (non-lifetime) broadening complicates the analysis. Ultrahigh resolution measurements with the 10 m grazing incidence spectrometer will facilitate the determination of widths for individual vibrational components for the simplest di-

atomic molecules. Such studies can then give information of the chemical dependence of total Auger transition probabilities.

Paper 19 presents the full argon L-emission spectrum. Most of the observed 123 lines are calibrated with an accuracy of better than 10 meV. The main mechanisms for producing the initial states of the X-ray satellites are the L_1-$L_{II,III}M$ Coster-Kronig and the $L_{II,III}M$ shake-off processes. The 10 keV electron excitation produces vacancies in the K-shell and the subsequent K-LL Auger deexcitation contributes also to the production of X-ray satellites. The probabilities of these creation mechanisms are discussed in some detail. The spectrum also shows strong low energy satellites, some of which have been identified as originating from interaction between the "normal" $3s2p^6$ final configuration and configurations of the type $3s^2 2p^4 n\ell$. Such semiinternal configuration interactions are also manifested in ESCA[15] and Auger[20] spectra pertaining to the inner 3s valence shell of argon.

V. Survey

In paper 20 some aspects of atomic and molecular soft X-ray studies are reviewed with special emphasis on the many parallels that exist with electron spectroscopy. A very good correlation is found between core level chemical shifts obtained from soft X-ray emission and ESCA spectra for a number of carbon and nitrogen containing molecules. Agreement is found to be within a few tenths of an eV. The small discrepancy is partly due to the difficulty of determining adiabatic energies in unresolved X-ray and core ESCA spectra. This matter is further elucidated in an appendix of paper 6, calculations of adiabatic and vertical X-ray and ESCA energies are reported in paper 5.

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